Great Lakes Binational Toxics Strategy
U.S. Challenge on Alkyl-lead:
Report on
Use of Alkyl-lead in Automotive Gasoline

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1.0 Introduction

On April 7, 1997, the United States Environmental Protection Agency (USEPA) and Environment Canada (EC) signed *The Canada-United States Strategy for the Virtual Elimination of Persistent Toxic Substances in the Great Lakes Basin* (Binational Strategy) (1). This agreement provided a framework for reducing or eliminating persistent toxic substances, especially those that bioaccumulate, from the Great Lakes Basin. The Binational Strategy established quantifiable pollution reduction challenges for the time frame 1997 to 2006 involving twelve "Level I" substances: aldrin/dieldrin, chlordane, DDT, mirex, toxaphene, alkyl-lead, benzo(a)pyrene, dioxins and furans, hexachlorobenzene, mercury, PCBs, and octachlorostyrene.

The Binational Strategy acknowledged and built on existing Canadian and U.S. regulatory programs that address the targeted substances, and the two governments will continue to cooperate on any new toxics reduction regulations. However, a cornerstone of the Binational Strategy is its reliance on voluntary measures to dramatically reduce pollutant discharges to the Great Lakes Basin. The Binational Strategy affirmed each country's commitment to virtually eliminating discharge of the targeted substances to the Great Lakes Basin and outlined a framework by which the countries can work together to achieve this objective.

1.1 Alkyl-lead Challenge

As part of the Binational Strategy, the United States and Canada have identified alkylated lead compounds (or alkyl-lead) as a "Level I" substance. Therefore, the virtual elimination of alkyl-lead, through pollution prevention and other incentive-based actions, is considered an immediate priority for both governments. EC and the USEPA have accepted the following challenges as significant milestones on the path toward virtual elimination of alkyl-lead emissions.

U.S. Challenge: Confirm by 1998, that there is no longer use of alkyl-lead in automotive gasoline. Support and encourage stakeholder efforts to reduce alkyl-lead releases from other sources.

Canadian Challenge: Seek by 2000, a 90 percent reduction in use, generation, or release of alkyl-lead consistent with the 1994 Canada-Ontario Agreement Respecting the Great Lakes Basin Ecosystem (COA).

This report addresses the first portion of the Alkyl-Lead Challenge for the United States — use of alkyl-lead in automotive gasoline. "Automotive gasoline" is defined as gasoline used in on-road vehicles (light and heavy gasoline vehicles, motorcycles, and gasoline trucks). Historically, on-road automotive sources in the U.S. have been the major contributors of lead emissions to the atmosphere (2). The second portion of the U.S. Alkyl-Lead Challenge — identifying and encouraging stakeholder efforts to reduce alkyl-lead emissions from other sources — will be the subject of a subsequent report.

1.2 Description of Alkyl-lead

Lead (CAS number 7439-92-1) is a naturally occurring, bluish-gray metal originating in the earth's crust. Its atomic number is 82, and it has an atomic (molecular) weight of 207.20. Its chemical abbreviation is Pb and other names for lead include C.I. 77575, C.I., pigment metal 4, KS-4, Glover, Lead S2, Olow (Polish), plumbum, and Omaha. Metallic lead is odorless, tasteless, and has no known physiological value. It does not dissolve in water and does not burn. The vast majority of lead chemical compounds are inorganic. However, lead can be combined with other chemicals to form lead compounds with very different characteristics from metallic lead (3). Alkyl-leads are by far the predominate type of organic lead compounds.

Alkyl-lead compounds are compounds in which a carbon atom of one or more organic molecules is bound to a metal atom. As with metallic lead, alkyl-lead compounds can occur naturally; however, most are man-made compounds used for various purposes (primarily as an "anti-knock" agent in gasoline). The most common alkyl-lead compound used as an anti-knock agent in gasoline is tetraethyl lead. Tetramethyl lead is also used as an anti-knock agent.

Tetraethyl lead is also referred to as lead tetraethide, tetraethyllead, and tetraethylplumbane and is commonly abreviated as TEL. It is a colorless, oily liquid, with a musty odor, and is typically dyed red, orange, or blue, depending upon its use. Tetramethyl lead, commonly abbreviated as TML, is also colorless and oily, with a musty odor. Table 1 summarizes additional properties of tetraethyl and tetramethyl lead.

Table 1. Properties of Tetraethyl Lead and Tetramethyl Lead

Property	Tetraethyl Lead (TEL)	Tetramethyl Lead (TML)
Chemical Formula	$Pb(C_2H_5)_4$	$Pb(CH_3)_4$
CAS Registry Number	78-00-2	75-74-1
Molecular Weight	323.45	267.35
Melting Point	-130 ^{o} C	-27 ^{o} C
Boiling Point	200 ^{o} C	108 ^{o} C
Liquid Density	1.65 g/cm^3	2.0 g/cm^3
Water Solubility	0.29 mg/L	17.9 mg/L

1.3 Health Effects of Lead Exposure

Alkyl-lead compounds added to gasoline combine with dichloroethane and dibromoethane or other lead scavengers during the combustion process to form lead oxides that are subsequently emitted as exhaust. Thus, very little alkyl-lead is emitted from gasoline combustion. The primary direct exposure routes to alkyl-lead is through inhalation of evaporative emissions during fuel refining, blending, and transportation, as well as during actual fueling or from dermal exposure to leaded gasoline.

Although alkyl-lead is generally not emitted from gasoline engine exhaust, the lead forms that are emitted add to total lead emissions. Inhalation of these airborne lead particles represents one mechanism by which humans can be exposed to lead. Oral exposure mechanisms include inadvertent ingestion of soil or dust that contains lead or ingestion of food or drinking water that has been contaminated by lead. Alkyl-lead is easily absorbed through the skin (4), while the possibility of dermal absorption of inorganic lead is considered to be low (5).

On a global basis, lead in gasoline has been estimated to contribute 95 percent of the lead

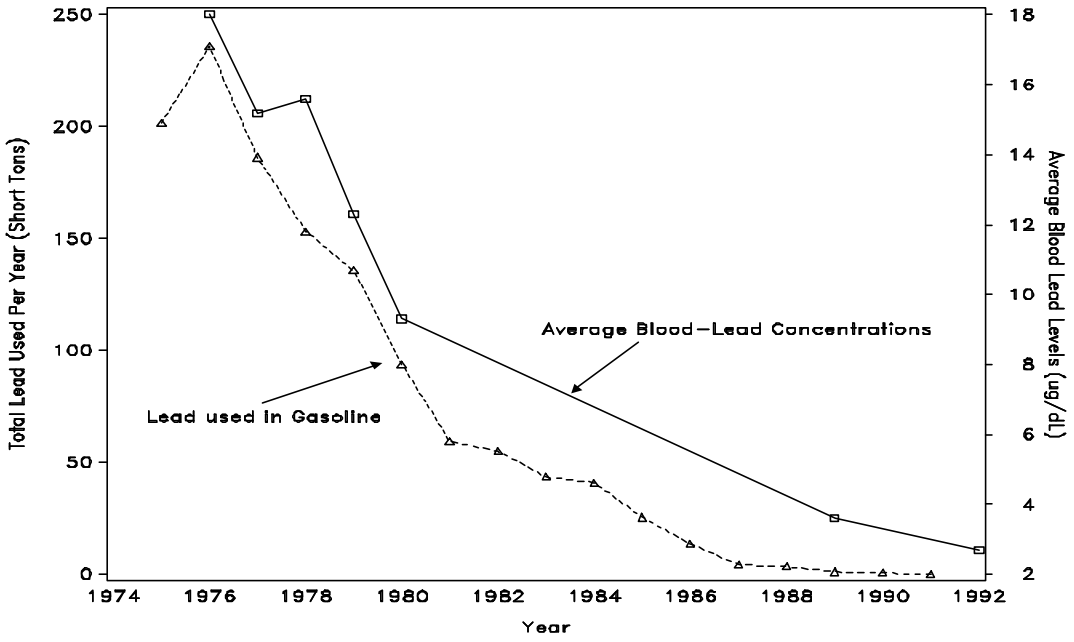

Figure 1. Relationship Between the Phase-out of Leaded Gasoline in On-road Vehicles and the Decline in Children's Blood-lead Levels in the U.S. [Figure Produced using data from National Health and Nutrition Examination Survey (NHANES), Unpublished Gasoline Production from the DOE's Energy Information Agency (EIA), and the Trends Procedure Document (8) for (lead content per gallon)]

air pollution found in the world's major cities (6). The United States, however, began phasing lead out of automotive gasoline in the 1970's. The gradual phase-out of lead in automotive gasoline has correlated with a dramatic decline in children's blood-lead concentrations as illustrated in Figure 1. Other factors, including the ban on the use of lead in house paint and reductions in dietary lead levels that took place during this time period (7), also likely contributed to the declining blood-lead concentrations. With the reduction in leaded gasoline and dietary intake, deteriorating lead-based paint in homes is now considered to be the primary source of lead exposure for U.S. children (9). Nevertheless, air emissions of lead from both on-road and nonroad vehicle emissions (as well as airborne sources such as lead smelters) contribute to childhood lead exposure through a variety of pathways including migration of lead from exterior soil to interior household dust.

Lead absorbed by the body is distributed through the blood to "soft tissues" (e.g., liver, kidneys, muscles, brain) and, over the course of several weeks, moves to and accumulates in "hard tissues" (e.g., bones, teeth). Lead stored in hard tissues can be mobilized back into soft tissues over time, particularly during periods of physiological stress. Lead in soft-tissues is thought to have a half-life of 35 to 40 days. Lead in hard tissues (about 90 percent of the total body-burden of lead) has a half-life of about 20 years (10).

The effects of lead are the same regardless of the source of exposure (inhalation, ingestion, or absorption). These effects are modulated by lead's distribution in the body, its affinity for various binding sites, and differences in cellular composition and structure within tissues and organs. Once lead enters the body, it interferes with normal cell function and with a number of physiologic processes. Lead primarily affects the peripheral and central nervous systems, the blood cells, and metabolism of vitamin D and calcium. Lead also causes reproductive toxicity (11).

Blood-lead concentration is a commonly used measure of body lead burden. An extensive body of research relates the health effects of lead exposure to blood-lead concentration. For example, lead-related reductions in intelligence, impaired hearing acuity, and interference with vitamin D metabolism have been documented in children at blood-lead concentrations as low as 10 to 15 μg/dL, with no apparent threshold. At higher exposure levels, these effects become more pronounced, and other adverse health effects are observed in a broader range of body systems. Increased blood pressure, delayed reaction times, anemia, and kidney disease may become apparent at blood-lead concentrations between 20 and 40 μg/dL. Symptoms of very severe lead poisoning, such as kidney failure, abdominal pain, nausea and vomiting, and pronounced mental retardation can occur at blood-lead levels as low as 60 μg/dL. At even higher levels, convulsions, coma, and death may result (3,12). Children are particularly at risk from lead exposure due to their low body weight and maturing neurological system.

2.0 Overview of Federal and State Regulations Governing Alkyl-lead

Alkylated lead compounds were included in gasoline soon after the anti-knock properties of alkyl-lead compounds were first discovered in 1921 (13). It was not until 1970, almost fifty years later, that the Clean Air Act (CAA) was introduced as the first legislative effort to reduce the amount of lead in gasoline. In the early 1970s, USEPA issued two regulations under the statutory authority of the 1970 CAA. First, USEPA required major gasoline retailers to begin selling one grade of unleaded gasoline by July 1, 1974. This mandate was primarily focused on preventing the deterioration, as a result of leaded gasoline, of emissions control systems (e.g., catalytic converters) in motor vehicles so equipped. In developing these regulations, USEPA first established the working definition of "unleaded" gasoline as "gasoline containing not more than 0.05 gram of lead per gallon and not more than 0.005 gram of phosphorus per gallon" [38FR1255, January 10, 1973]. USEPA issued a regulation calling for the gradual phase-out of leaded gasoline. The schedule for reduction of lead content in automobile gasoline was 1.7 grams per gallon (g/gal) in 1975, to 1.4 g/gal in 1976, 1.0 g/gal in 1977, 0.8 g/gal in 1978, and 0.5 g/gal in 1979 [38FR33741, December 6, 1973]. Subsequent regulations reduced the allowable lead content to 0.1 g/gal in 1986 [50FR9397, March 7, 1985], and prohibited leaded gas use after 1995 [61FR3837, February 2, 1996].

Most recently, alkylated lead compounds have been regulated under the 1990 Clean Air Act Amendments (CAAA). The following components of the 1990 CAAA relate to alkyl-lead:

1. Emissions for Nonroad Vehicles. Section 213 of the 1990 CAAA requires USEPA to consider regulating emissions from off-highway vehicles[1] (construction equipment, boats, farm equipment, lawn equipment, etc.). Currently, these vehicles are permitted to use leaded gasoline, but may be regulated in the future.

2. Misfueling with Leaded Gasoline. Section 211(g) of the 1990 CAAA prohibits misfueling vehicles built after 1990 (or vehicles designated solely for unleaded gasoline) with leaded gasoline.

3. Prohibition on the Use of Leaded Gasoline in On-Road Vehicles. Section 211(n) of the 1990 CAAA states: "After December 31, 1995, it shall be unlawful for any person to sell, offer for sale, supply, offer for supply, dispense, transport, or introduce into commerce, for use as fuel in any motor vehicle (as defined in Section 219(2)) any gasoline which contains lead or lead additives." This provision applies only to on-road vehicles. Enacting regulations were promulgated [61FR3837, February 2, 1996].

4. Prohibition on Production of Engines Requiring Leaded Gasoline. Section 218 of the 1990 CAAA requires USEPA to promulgate rules that prohibit the "manufacture, sale, or introduction into commerce of any engine that requires

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[1] Fuels for Race Cars or "Competition Use Vehicles" are exempted from regulation under the Clean Air Act.

leaded gasoline." Further, these rules apply to all motor vehicle engines and nonroad engines manufactured after the 1992 model year.

5. Identification of Sources of Alkyl-Lead. Section 112(c)(6) of the 1990 CAAA requires USEPA to identify sources of alkyl-lead (and six other chemicals). The identified sources must account for at least 90 percent of the aggregate emissions for alkyl-lead. In response, USEPA developed emission inventories of known sources of each pollutant and added two source categories on April 3, 1998: (1) open burning of scrap tires, and (2) gasoline distribution Stage I aviation (including evaporative losses associated with the distribution and storage of aviation gas containing lead).

Thus, the sale or use of gasoline containing alkyl-lead (greater than 0.05 grams of lead per gallon) is now prohibited in on-road vehicles [40CFR Part 80.22].

3.0 Status of Domestic Use of Gasoline Containing Alkyl-lead in On-road Vehicles

While the use of leaded gasoline in on-road vehicles is prohibited by the 1990 CAAA, the production of leaded gasoline for other uses was not prohibited. For example, leaded gasoline is a predominant fuel in the general aviation (piston engine) industry, and it is also used in farm machinery and race cars. However, the introduction of unleaded gasoline in the late 1970s and the enactment of the 1990 CAAA has caused production volumes of leaded gasoline to fall dramatically. Consequently, lead emissions from the use of leaded gasoline in on-road vehicles have also fallen dramatically.

3.1 Production of Gasoline Containing Alkyl-lead

The production of gasoline containing alkyl-lead has greatly diminished. As seen in Figure

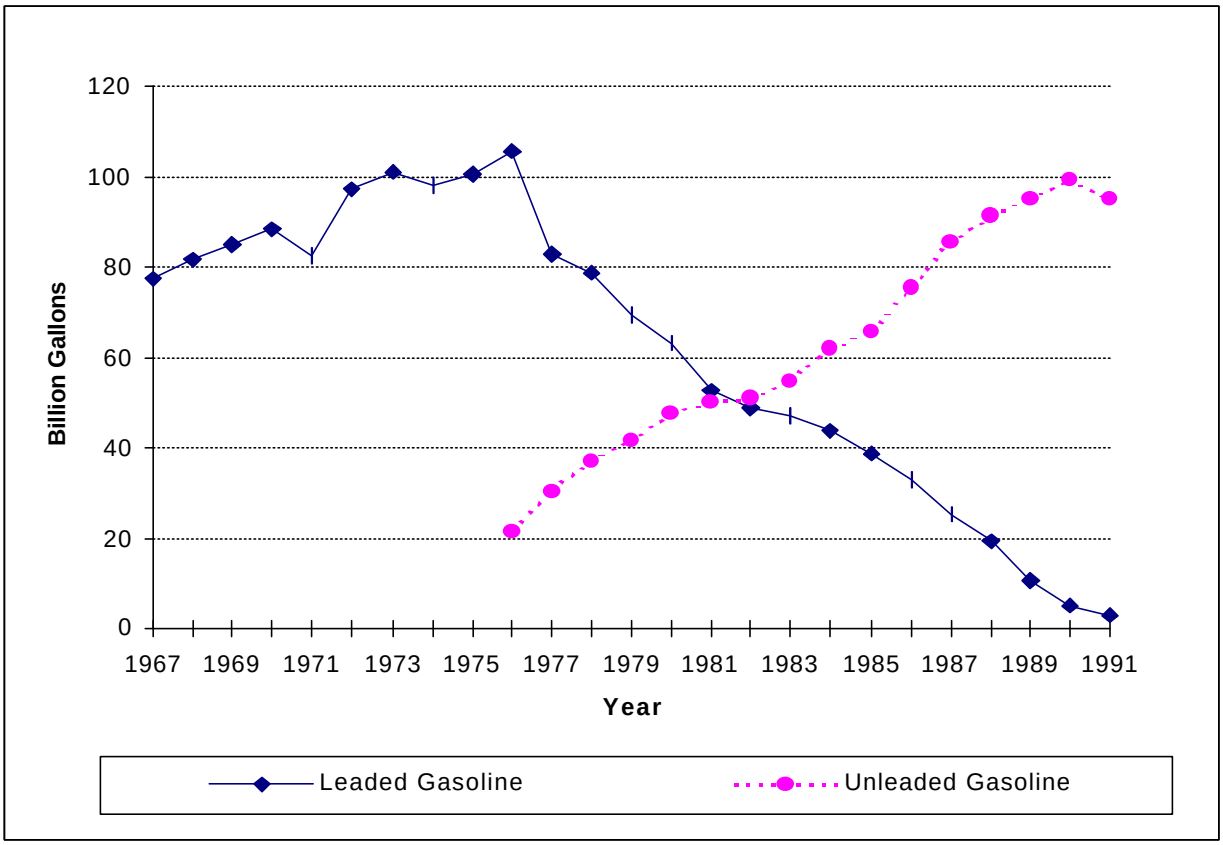

Figure 2. Summary of Unleaded vs. Leaded Gasoline Production 1967-1991.
[Figure produced using unpublished data, USEPA 1991 (14).]

2, the production of leaded gasoline has decreased from 77.5 billion gallons in 1967 to 3.1 billion gallons in 1991 (14), or to 3% of all gasoline produced.

Conversely, the production of unleaded gasoline has risen sharply. In 1991, 94.9 billion gallons of unleaded gasoline were produced, which represents approximately 97 percent of all gasoline

produced. To complete the leaded gasoline phase-out picture, it would be desirable to obtain more recent production information for leaded and unleaded automotive gasoline.

3.2 Lead Emissions

The overall amount of lead emissions (all forms of lead and lead compounds, including alkyl-lead) in the U.S. has decreased by two orders of magnitude between 1970 (220,869 short tons emitted) and 1996 (3,869 short tons emitted) (15) Figure 3 summarizes estimates of total lead emissions by year. Most notable in Figure 3 is

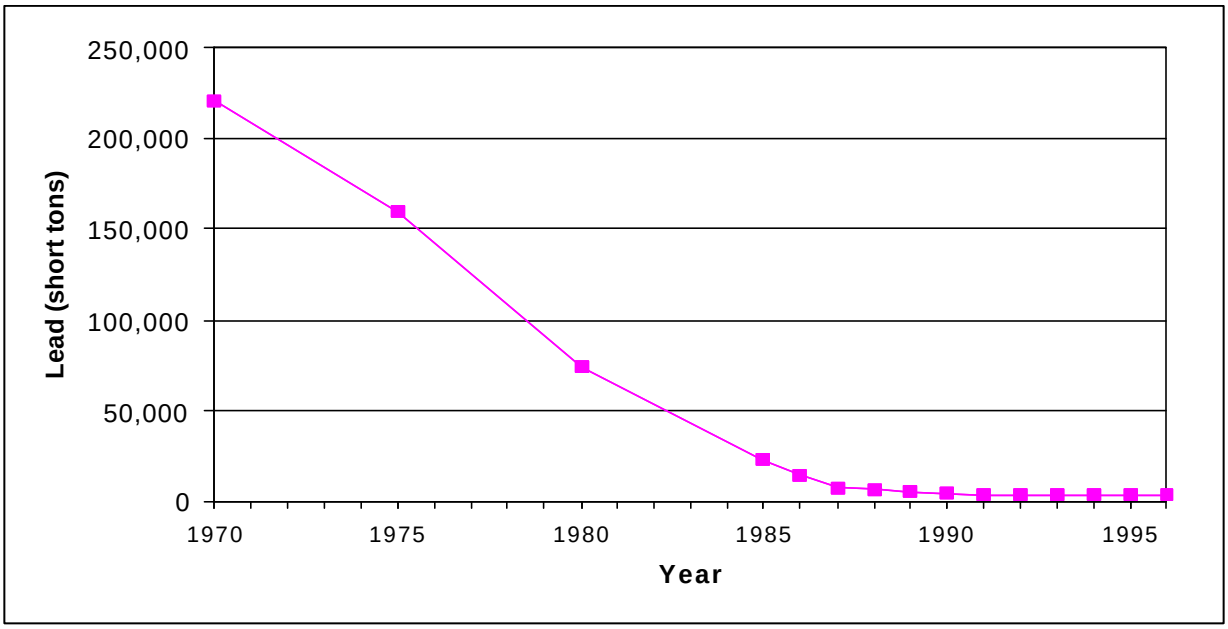

Figure 3. Total Lead Emissions (Short Tons) by Year.
[Figure reproduced from National Air Pollutant Emission Trends Report, 1900-1996 (15).]

that the greatest reduction in lead emissions occurred between 1970 and 1985. This large reduction is a direct result of the regulated phase-out of leaded gasoline (reductions in both the lead content per gallon and the total gallons produced) and the increased availability of unleaded gasoline (3). Currently, there are several major sources of airborne lead emissions[2], including bulk production plants for aviation gasoline, nonroad vehicles, waste incinerators, metal processing, and other fuel combustion (e.g., electrical utility, industrial). As seen in Figure 4, on-road emissions, the predominant emissions source in the 1970s and 1980s, contributed less than

[2] Through the combustion process in automotive engines, alkyl-lead compounds combine with fuel scavengers to form lead oxides. Alkyl-lead is the only known significant source of lead in gasoline. Typically, only a very small percentage (0.2%-0.4%) of alkyl-lead is exhausted uncombusted when driving at constant speeds (16). Therefore, estimates of the total lead emitted as exhaust from on-road vehicles will be used to characterize the decline in use of leaded gasoline in on-road vehicles.

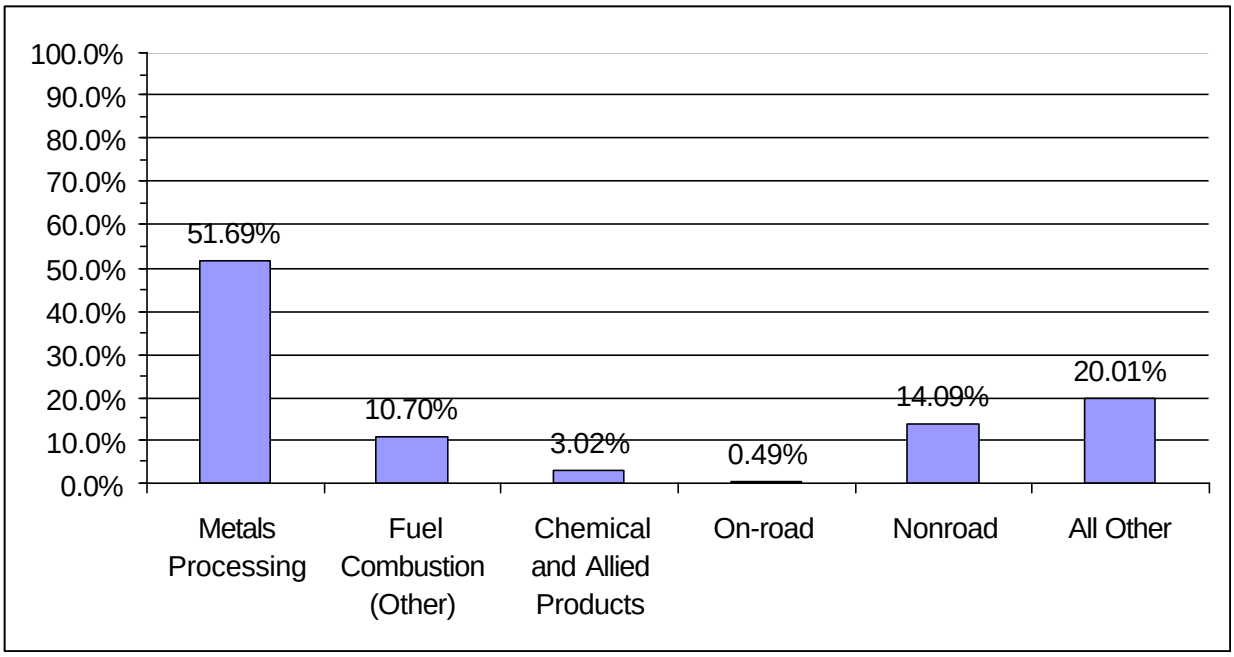

Figure 4. Percentage of 1996 National Emission Estimates by Source (Short Tons). [Figure produced using data from National Air Pollutant Emission Trends Report, 1900-1996, EPA 1997 (15).]

one-half of one percent to the total emissions in 1996 (2, 15). In 1996, metals processing was estimated to be the predominant source of lead emissions. Therefore, not only have total lead emissions been reduced, but the relative contribution of on-road vehicles has also been reduced. With the continued implementation of provisions of the 1990 CAAA, this trend is expected to continue.

Table 2 summarizes the information contained in Figures 3 and 4. Emissions of lead compounds from on-road vehicles were estimated by USEPA to be approximately 19 tons in 1996. However, this estimate does not imply a widespread use of leaded gasoline as a fuel source for on-road vehicles. Rather, this emission estimate incorporates the trace amount of lead remaining in unleaded gasoline. This trace amount of lead is due to the sharing of distribution systems utilized by gasoline manufacturers for the production of leaded and unleaded gasoline and residual amounts of lead in crude oil. USEPA has determined that requiring manufacturers to eliminate this trace amount is not economically feasible. As production of leaded gasoline has decreased, so too has the trace amount of lead in unleaded gasoline.

Table 2. 1995 and 1996 National Lead Emissions by Source Category

Source Category	Emissions (short tons)	
	1995	1996
Metals	2,067	2,000
Primary lead production	674	636
Secondary lead production	432	400
Gray iron production	366	339
All other	595	625
Fuel combustion other	414	414
Chemical and Allied Products (lead oxide and pigments)	144	117
On-road	19	19
Nonroad[(a)]	545	545
Nonroad gasoline	0	0
Aircraft	545	545
All other	754	774
Total	3,943	3,869

[Table reproduced from Table 2-1 in the National Air Pollutant Emission Trends Report, 1900-1996, EPA 1997.]

(a) EPA did not develop estimates for Nonroad emissions (other than those for aviation) because they were deemed to be extremely low relative to other sources.

4.0 Compliance and Enforcement

Because leaded gasoline still is produced in the United States, is being used in nonroad vehicles (primarily as aviation fuel, but also in farm machinery and race cars), and is dispensed by private citizens, it is possible that illegal misfueling occurs. Historically, USEPA's Office of Enforcement has not found this to be the case in public gasoline service stations. In previous years, USEPA's Office of Enforcement screened for lead during routine inspections at service stations. However, as leaded gasoline became increasingly scarce, the number of violations related to the misuse of leaded gasoline dropped precipitously (see Table 3) (17). As a result of finding virtually no cases of misfueling, USEPA's Office of Enforcement no longer routinely screens for lead as part of the typical inspection process. It does continue to test for lead on a case-by-case basis if illegal misfueling is suspected. Typically, very few cases of suspected misfueling with leaded gasoline are investigated in a given year. No documentation of investigation of misfueling of leaded fuel intended to fuel farm machinery or racing cars was found for this report.

Although it is possible for misfueling of on-road automobiles to occur using leaded racing gasoline, such misfueling, if it occurs at all, is likely to be rare. Limited supply, limited distribution, much higher cost, incompatibility with emission control systems on production automobiles, and limited performance benefits in production automobiles designed for unleaded gasoline all weigh against use of leaded racing gasoline in on-road automobiles.

Table 3. Violations Issued for Excess Lead-levels in Gasoline
[Source: USEPA (17)]

Year	Number of Service Station Inspections	Number of Violations Issued	Violation Rate
1980	5,021	83	1.65%
1981	10,179	73	0.72%
1982	10,266	60	0.5%
1983	9,896	41	0.41%
1984	4,652	24	0.52%
1985	5,363	30	0.56%
1986	5,363	8	0.15%
1987	9,003	4	0.04%

5.0 Conclusions

The 1990 Clean Air Act Amendments prohibit the use of leaded gasoline as fuel for on-road automotive use. As a result of this prohibition and earlier CAA regulations, the production of leaded gasoline and its use in on-road vehicles has declined dramatically, as have estimates of lead emissions resulting from on-road vehicles. It is clear that the vast majority of on-road vehicles use unleaded gasoline as their primary fuel. This can be verified by examining emission and production estimates. In particular, the amount of leaded gasoline produced is not sufficient to serve as fuel for a significant number of on-road vehicles. Further, emissions of lead have decreased since leaded gasoline was phased out, and on-road vehicles are estimated by USEPA to account for less than one-half of one percent of the total amount of lead emitted in 1996.

Leaded gasoline is still legally produced and used as fuel for a variety of other vehicles in the United States (e.g., aviation, farm machinery, nonroad automotive). Although illegal misfueling of on-road vehicles with leaded gasoline is possible, it is likely to be rare, if it occurs at all.

Based on the above, it is concluded that alkyl-lead has been virtually eliminated from use in automotive gasoline. Further confirmation should be sought by collecting up-to-date leaded gasoline production data. This could be done when a detailed inventory of all sources of alkyl-lead is conducted as part of the Great Lakes Binational Toxics Strategy 4-Step Process to virtual elimination.

6.0 References

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